Small-Angle Scattering from Micellar Solutions

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A b s t r a c t

Micellar solutions are the suspension of the colloidal aggregates of the surfactant molecules in aqueous solutions. The structure (shape and size) and the number density of these aggregates, referred to as micelles, depend on the molecular architecture of the surfactant molecule, presence of additives, and the solution conditions such as temperature, concentration etc. Small-angle scattering is a powerful technique to study the micellar solutions. Depending on the radiation used there are two well-established techniques, namely, small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS). These two techniques provide complementary information on the micelles. We have made a combined use of SANS and SAXS to the study of the counterion condensation in ionic micelles.

Introduction

SURFACTANT MOLE-cules consist of a polar hydrophilic head group and a long hydrophobic chain connected to the head group. The coexistence of the two opposite types of behavior (hydrophilic and hydrophobic) in the same molecule leads to the self-aggregation of the surfactant molecules when dissolved in water. The aggregates are called as micelles. The typical size of a spherical micelle is about 50 Å and is made up of about 100 surfactant molecules. A schematic representation of a surfactant molecule and a spherical micelle is shown in Figure 1. The micelles are formed by the delicate balance of opposing forces: the attractive tail-tail hydrophobic interaction provides the driving
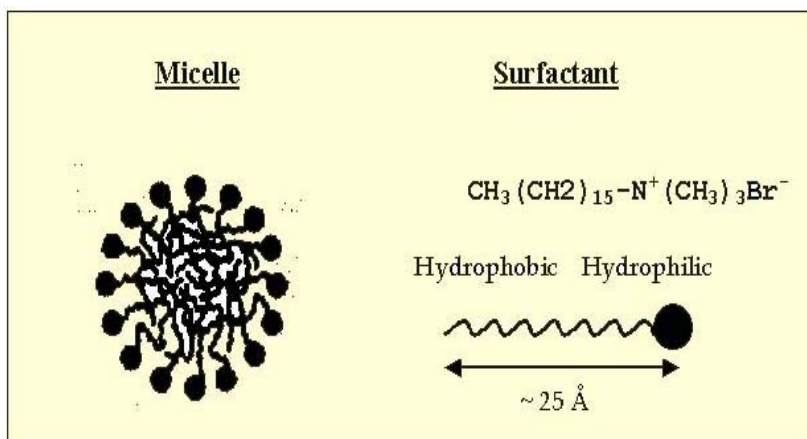

Fig. 1 Schematic of a surfactant molecule and a spherical micelle.

force for the aggregation of the surfactant molecules, while the electrostatic repulsion between the polar head groups limits the size that a micelle can attain. As a result, the characteristics of these aggregates are easily controlled by the small changes in chemical structure of the surfactant molecule and the solution conditions such as concentration, temperature and ionic strength. The aggregates

formed are of various types, shapes and sizes such as spherical or ellipsoidal, cylindrical or thread-like micelle, disk-like micelle, membrane and vesicles [1]. The study of formation of these different structures is important as the surfactant solutions are widely used in various household, industrial and research applications.

Surfactant molecules such as cetyltrimethyl-ammonium bromide (CTABr) ionize in aqueous solution and the corresponding micelles are aggregates of CTA^+ ions. The micelle is charged and is called an ionic micelle. The Br^- ions, known as counterions, tend to stay near the CTA^+ micellar surface. The shape, size, fractional charge of the micelle and the intermicellar interaction depend on the nature of these counterions [2]. Since the works of Oosawa [3] and Manning [4], the concept of counterion condensation is widely accepted in the field of linear polyelectrolytes. It has been shown that when the charge density on an infinitely long cylinder is increased beyond a critical value, counterions condense around the cylinder so as to reduce the effective charge density to the critical value. Similar concepts have also been used in colloidal suspensions made of spherical charged colloids [5]. The counterions located at short enough distances from the colloidal surface feel a very strong electrostatic attraction compared with the thermal energy k_BT and these counterions are called as bound to or condensed on the colloid. In ionic micellar solutions, the counterion condensation plays very important role to decide the effective charge on the micelle and hence the formation, structure and interaction of the micelles [6].

The scattering techniques small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS) in combination provide a direct method to study the counterion condensation in ionic micelles. While neutron scattering in micellar solutions is from the core of the micelle, x-rays are largely scattered by counterions, especially when the counterion has a large atomic number (e.g. Br^-). The neutron scattering intensity from the counterion distribution is negligible in comparison to that

from the core. Thus neutrons see the core of the micelle and x-rays give information relating to the counterion condensation around the micelle [7].
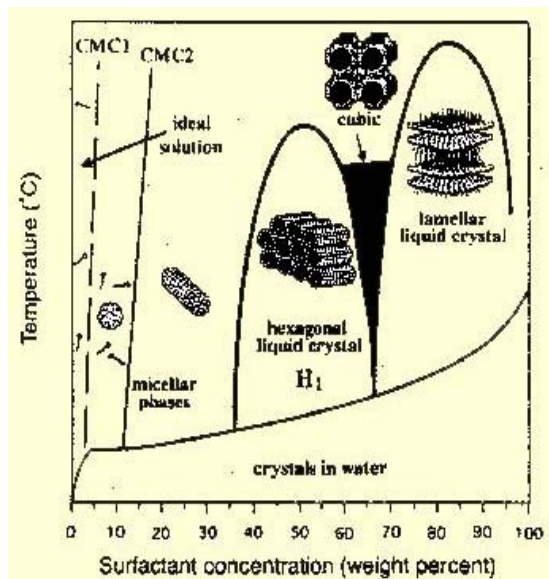

Fig. 2 Phase diagram of ionic surfactant CTABr in water.

Figure 2 shows the phase diagram for ionic surfactant CTABr in water [8]. At low surfactant concentrations, CTABr forms the small spherical micelles. The spherical micelles transform to long rod-like as the concentration is increased. At higher concentrations, different liquid crystalline structures are formed. The above variety of structures in the phase diagram strongly depends on the counterion condensation. Herein, we discuss the small-angle scattering as a method to study the counterion condensation in ionic micelles.

Small-angle Scattering

The small-angle scattering intensity $I(Q)$ as a function of scattering vector Q ($=4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident radiation) for a micellar solution can be expressed as [9]

$$I(Q) = nP(Q)S(Q) \qquad (1)$$

where n is the number density of the particles. $P(Q)$ is the intraparticle structure factor and depends on the shape and size of the particles. $S(Q)$ is the interparticle structure factor and is decided by the spatial distribution of the particles. $P(Q)$ is given by the integral

$$P(Q) = \left| \int (\rho(r)-\rho_s) exp\,Ii\boldsymbol{Q}.\boldsymbol{r})dr \right|^2 \qquad (2)$$

In the simplest case of a monodispersed system of homogeneous particles with a radius R, $P(Q)$ is given by

$$P(Q) = (\rho - \rho_s)^2 V^2 \left[\frac{3J_1(QR)}{QR} \right]^2 \qquad (3)$$

where $V = (4/3)\pi R^3$, ρ_s is the scattering length density of the solvent and ρ is the mean scattering length density of the particle.

The expression for $S(Q)$ depends on the relative positions of the particles. In case of isotropic system, $S(Q)$ can be written as

$$S(Q) = 1 + 4\pi n \int (g(r)-1) \frac{\sin Qr}{Qr} r^2 dr \qquad (4)$$

where $g(r)$ is the radial distribution function. $g(r)$ is the probability of finding another particle at a distance r from a reference particle centered at the origin. The details of $g(r)$ depend on the interaction potential $U(r)$ between the particles. The term $(\rho-\rho_s)^2$ is referred as a contrast factor. The above equations are valid both for the SAXS and the SANS experiments. The contrast factor, however, depends on the radiation used [10]. The values of ρ and ρ_s depend on the chemical composition of the micelle and the solvent and are different for neutrons and x-rays. The differences in ρ values for neutrons and x-rays arise from the fact that while neutrons are scattered by the nucleus of an atom, the x-rays are scattered by the electron clods around the nucleus. It is seen that as one goes across the periodic table, the neutron scattering lengths vary in a random way and the x-ray scattering lengths increase with the atomic number of the atom. For example, unlike x-rays where ρ_s (H_2O)

$= \rho_s$ (D_2O), the values of ρ_s changes significantly for neutrons when solvent is changed from H_2O to D_2O. X-rays are scattered more strongly from heavy elements (e.g. Cl^-, Br^- etc.) as compared to light elements such as C, H etc.

Results

Comparison of SANS and SAXS data from ionic micellar solutions

Figure 3 shows the comparison of SANS and SAXS data on 100 mM CTABr micellar solution. Both these data show a correlation peak at $Q \sim 0.05$ $Å^{-1}$, which is due to peak from the interparticle structure factor $S(Q)$ [11]. The fact that the average distance between the micelles mainly decides position of the correlation peak, it is independent of the radiation used. The peak usually occurs at $Q_m \sim 2\pi/d$, where d is the average distance between the micelles and Q_m is the value of Q at the peak position.
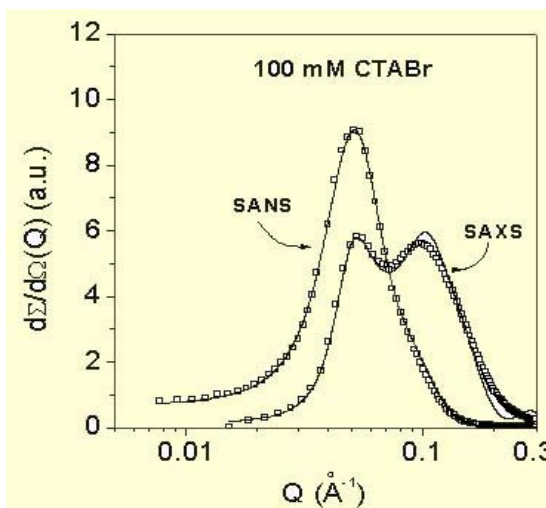

Fig. 3 Comparison of SANS and SAXS data for 100 mM CTABr

The second peak in the SAXS data arises from scattering of shell-like structure of the condensed counterions around the micelles. The analysis of SANS data using Eq. (1) determines the shape and size of the micelles. It is found that the micelles are prolate ellipsoidal with the semimajor axis (a) = 40.2 Å and semiminor axis

(b=c) = 24.0 Å, respectively. The counterion condensation per surfactant molecule on the micelles has the value about 77 %. The above structure and interaction information about the micelles as obtained from SANS is used to fit the SAXS data and the thickness of the condensed counterions around the micelles is obtained as an additional parameter. The calculated value of the thickness over which the Br- counterions are condensed is 4.2 Å.

Size dependence of the counterions and micelles on the counterion condensation

It has been known that depending on the size of the counterions, the phase diagrams of the similar ionic surfactants have been very different. For example, while the ionic surfactant cetyltrimethylammonium bromide (CTABr) shows sphere to rod-like transition of micelles with the increase in the surfactant concentration, the micelles of cetyltrimethylammonium chloride (CTACl) remain spherical even up to very high surfactant concentrations. This also leads to the different liquid crystalline structures of the surfactants at higher concentrations.

To explain the above differences, Figure 4 shows the comparison of SANS and SAXS data for CTABr and CTACl micellar solutions. SANS suggests the formation of much smaller micelles for CTACl than CTABr [12]. This is explained due to the lower condensation of Cl- counterions on the micelles. On the other hand, SAXS data suggest that counterions be condensed over larger thickness for CTACl micelles. When surfactant concentration is increased, SANS data show that counterion condensation decreases for CTABr micelles and it remains more or less same for CTACl micelles [13]. In terms of SAXS data, it shows that the counterions maintained to remain over same thickness for CTABr micelles and the thickness increases for CTACl micelles.

Similar results to those of the varying counterions are also obtained when the size of micelles is varied. It is seen from the SANS data that counterion condensation on the ionic micelles increases with the increase in the size of micelle [14]. This is term of SAXS data shows that the counterions get condensed over smaller thickness when the size of micelles is increased.
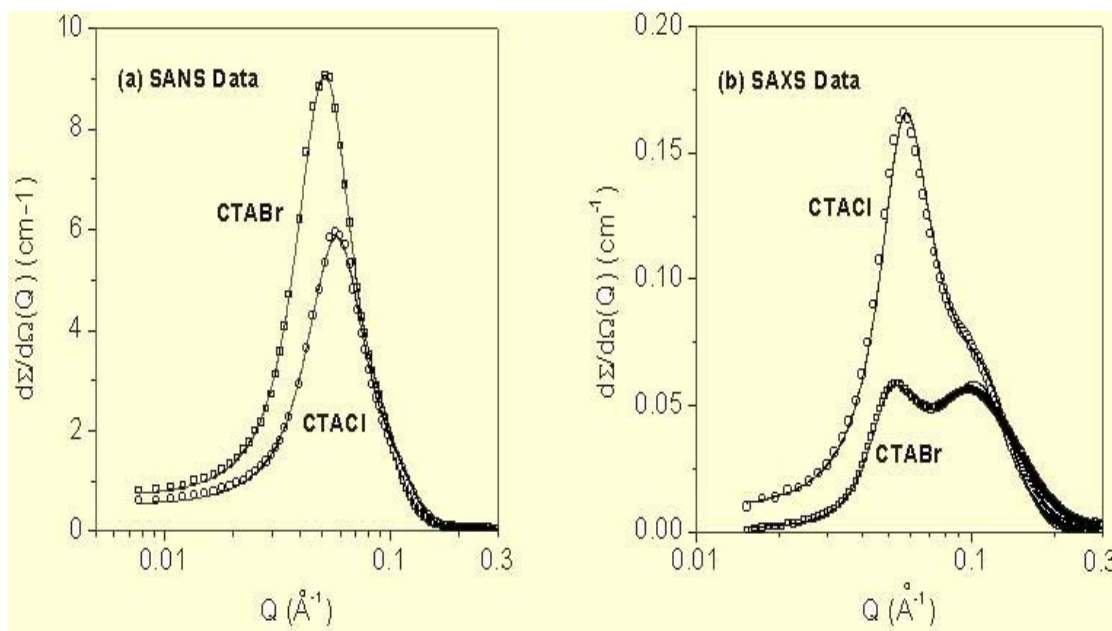

Fig. 4 Comparison of (a) SANS and (b) SAXS data for 100 mM CTABr and CTACl micellar solutions.

Selective counterion condensation in ionic micelles

The effect of addition of salts KBr and KCl to the ionic micellar solutions of cationic surfactant (e.g. CTABr or CTACl) is quite different [15]. In terms of counterion condensation, this suggests the differences in the condensation of Br^- and Cl^- ions that take place on the charged micelles. It is interesting to compare the structure in the equimolar surfactant to salt micellar solutions of CTABr/KCl and CTACl/KBr systems [16]. Figure 5 (a) shows the SANS data from equimolar surfactant to salt CTABr/KCl and CTACl/KBr micellar solutions. These systems have common in them the same number of surfactant CTA^+ ions and as well as Br^- and Cl^- counterions. For comparison, the data from 100 mM CTABr and CTACl micellar solutions without salt are also shown in Figure 5 (a). It is observed that the counterion condensation is more effective in CTACl/KBr than CTABr/KCl. We believe this is due to selective condensation of the counterions around the micelles [16]. In CTABr/KCl, Br^- counterions from the dissociated CTABr molecules are condensed on the CTA^+ charged micelles. The condensation of Cl^- ions of the salt KCl takes place around the condensed Br^- ions. However, in CTACl/KBr, Cl^- counterions of the CTACl molecules are replaced by Br^- ions of the KBr in the micelle. This is expected since Cl^-

ions are less effective than Br^- to neutralize the charge on the micelles.

The above SANS results are directly confirmed by the SAXS experiments, where the scattering data depending on the condensed counterions is expected to be different. Figure 5 (b) shows while the SAXS data of CTABr and CTACl are very different the data for CTABr/KCl and CTACl/KBr are quite similar. The small differences in the SANS or SAXS data of CTABr/KCl and CTACl/KBr can be explained in terms of a small fraction of condensed Cl^- counterions in CTACl/KBr, which are not replaced by the Br^- counterions. This provides slightly higher condensation of Cl^- counterions on the micelles of CTACl/KBr than CTABr/KCl, otherwise these two systems have similar counterion condensation of Br^- and Cl^- ions around them.

In summary, small-angle scattering is an ideal method to the study of the micellar solutions. The use of SANS and SAXS provide complementary information on the micelles. The combined experiments of these two techniques have been used to study the counterion condensation in ionic micelles. While neutron scattering in micellar solutions is from the core of the micelle, x-rays are largely scattered by counterions, especially when the counterion has a large atomic number (e.g. Br^-).
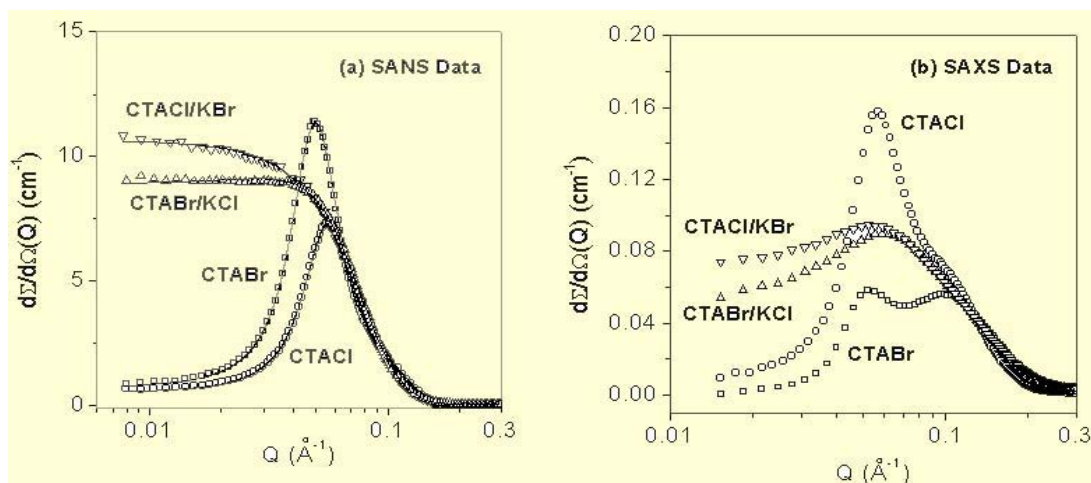

Fig. 5 (a) SANS and (b) SAXS data from equimolar surfactant to salt micellar solutions of CTABr/KCl and CTACl/KBr. For comparison the data from pure CTABr and CTACl micellar solutions are also shown.

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